Research paper

The effect of montmorillonite clay in alginate gel beads for polychlorinated biphenyl adsorption: Isothermal and kinetic studies

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A B S T R A C T

Beads of alginate montmorillonite have been used as sorbent for polychlorinated biphenyls from aqueous solutions. The structure and the differences between the different beads were established by IR spectroscopy (FT-IR). The adsorption at 25 °C has been studied in a batch system, following its kinetics and assessing adsorbent dose, initial PCB concentrations, and pH effects. The results show that increasing the initial concentration of the PCBs and the adsorption time favored the adsorption. Adsorption isotherm data were modeled using Chapman, Freundlich and Langmuir adsorption isotherms and the appropriate parameters were calculated. Adsorption of trichlorobiphenyls on alginate–montmorillonite beads followed a Freundlich isotherm type model, while adsorption of tetra-, penta-, and hexachlorobiphenyls displayed a sigmoid-shaped (S-type) isotherm fitting the Chapman sigmoidal equation with the highest non-linear R² values among the three tested models. By comparing the percentage adsorptions using the same number of beads (same volumes), best removals were obtained by using alginate montmorillonite beads. Kinetic models were investigated to determine the mechanism of adsorption showing a best fit for the pseudo-second order model (R² from 0.998 to 0.982). Moreover, to underline the effect of montmorillonite in alginate gel beads, we have compared the isothermal adsorption curves between alginate montmorillonite and alginate beads.

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1. Introduction

The industrial growth and population increase have resulted in the release of different pollutants in the environment and the treatment of effluents has become a challenging topic in environmental sciences. Hydrophobic organic compounds (HOCs) consist of wide classes of persistent contaminants in environmental matrices, particularly in water (Pace and Barreca, 2013) soils (Orecchio, 2010a, 2010b; Van Jaarsveld et al., 1997) and sediments (Barreca et al., 2014a; Orecchio et al., 2010).

Polychlorinated biphenyls (PCBs), an example of HOCs, are a class of compounds containing from one to ten chlorine atoms bound to a biphenyl molecule (Frame et al., 1996).

The low aqueous solubility of this class of contaminants is a fundamental feature that is directly related to their equilibrium concentration in the aqueous phase, which controls the toxicity (Giesy and Kannan, 1998), sorption, bioaccumulation and biodegradation (Sinkkonen and Paasivirta, 2000). In fact, several PCB congeners are resistant to degradation, which allows them to persist in the environment for long times and become widespread via atmospheric and water transport mechanisms (Meneses et al., 2002; Stevens et al., 2001).

The PCB determination in environmental samples may be carried out by traditional methods (Method 1668C U.S. Environmental Protection Agency, April 2010) or using innovative and environmentally friendly techniques (Barreca et al., 2013).

PCBs were used for industrial purposes from the 1930s until the late 1970s. In Europe, although their industrial production ended in the late 1970s, PCBs’ presence in the environment is still significant due to inconsiderate disposal activities or leakage from industrial facilities and their removal from aqueous matrices is a topic of great environmental interest.

The use of clay such as montmorillonite for PCB removal from water solutions has been widely discussed in the past (Delle Site, 2001), but because of physical properties such as low water permeability, the montmorillonite use for decontaminations is still under investigation (Brigante et al., 2013).

Efforts are therefore still needed in order to produce low cost adsorbents that are versatile e.g. having high adsorption capacity of inorganic and/or organic pollutants.

Due to their economic feasibility, adsorption–regeneration properties and mechanical strength, polymeric adsorbents have been recently used.
as an alternative to conventional materials such as activated carbon. Several studies report the use of chitosan in the form of flakes, powder or with hydrogel beads or clay-based composites for inorganic and organic pollutant adsorption (Bleiman and Michaël, 2010; Celis et al., 2012; Chatterjee et al., 2010; Chia Yang and Hsiung Hon, 2009; Yamani et al., 2012; Zhu et al., 2010).

Chitosan, a poly(D-glucosamine), is obtained from chitin by deacetylating its acetamide groups with a strong alkaline solution. Chitin is a natural polymer extracted from crustacean shells, such as prawns, crabs, shrimps, as well as insects and fungal biomass. Chitosan has already been described as a suitable natural polymer for the removal of phenolic compounds, through chelation involving the amino and hydroxyl groups in the glucosamine unit (Inoue et al., 1996; Juang and Ju, 1998; Rhee et al., 1998). Sodium alginate, a natural polymer extracted from seaweed, has been used in environmental decontamination, including the removal of organic compounds from water. For example, alginate filled with montmorillonite was used for the removal of nitrophenol and as a pesticide adsorbent (Barreca et al., 2014b; Ely et al., 2009; Fernández-Pérez et al., 1999; Gerstl et al., 1998). Sodium alginate exhibits a sol–gel transition when subjected to cation exchange, e.g. when a calcium ion replaces two sodium cations. This material is biocompatible, economical and can be easily prepared by encapsulation (Kittinaoaravat et al., 2010).

Alginates are common and well-known support materials in biosciences applications (Bayramoglu et al., 2002) and are now used in the environmental field (Aguzzi et al., 2007; Silva et al., 2008).

Aluminoisicates (natural or modified) have been tested since more than 40 years ago in the removal of toxic metals or organic pollutants (Bailey et al., 1968; Griffin and Shimp, 1976; Montarges et al., 1998) from aqueous solutions due to favorable surface properties, availability, and environmental and economical considerations. Most of these materials are not suitable for extensive process utilization due to the lack of a spherical or uniform shape. Consequently, encapsulation of these materials in a polymeric matrix, such as calcium alginate, can be envisaged as an alternative technique to resolve these issues (Jing et al., 2013).

Hybrid hydrogels, which are water-swollen materials that maintain a distinct three-dimensional structure and are composed of polymeric and inorganic components, have gained great attention as effective adsorbents due to their high water retention and low cost. Clays supported on calcium alginate beads have been reported to improve the mechanical and thermal stabilities of the beads and to simplify the separation procedures compared to the use of natural clays (Cavallaro et al., 2013).

In this report we present adsorption studies for PCBs at different chlorination grades onto alginate and alginate-clays (Cavallaro et al., 2013). The mechanisms responsible for analyte adsorption.

2.1. Chemicals

The work solutions were prepared by drying and re-dilution from stock internal standard solutions of PCB mixture (1 mg L⁻¹) (Chemical Research WELEPA-1668IS). In detail, the components of PCB mixture are reported in Table 1. For PCB analysis, stock standard solution containing a mixture of analytes was purchased from Chemical Research.

Stock internal standard solutions of PCBs (a mixture of PCB28, PCB52, PCB95, PCB101, PCB99, PCB81, PCB110, PCB77, PCB151 PCB149, PCB123, PCB118, PCB114, PC146, PCB153, PCB105) were prepared (100 μg L⁻¹) in hexane from commercial standard nonane solutions (1 mg L⁻¹) (Chemical Research O2S130111-01) by drying and re-dilution.

Stock congener solutions of PCBs were prepared at different concentrations in hexane from commercial standard isooctane solutions (10 mg L⁻¹) (Chemical Research 02S130111-01) by drying and re-dilution. Both stock internal and commercial standard solutions were stored in a refrigerator (4 °C).

2.2. Preparation of alginate and alginate–montmorillonite beads

Alginate beads were prepared according to the procedure reported in literature (Silva et al., 2008).

In turn, alginate montmorillonite beads were prepared by adapting the ionic gelation method (Bee et al., 2011; Guibal et al., 2010; Vincent et al., 2008).

K10 montmorillonite (8 g) was dispersed in 50 mL of Milli-Q water under continuous stirring. A 2% (w/v) Na-alginate suspension was prepared by dissolving 1 g of sodium alginate in Milli-Q water (50 mL). The alginate suspension (50 mL) was added to the suspension of montmorillonite and the mixture was stirred for 2 h. Once the mixture appeared homogeneous, it was forced through a micropipette tip by a peristaltic pump and the resulting gel droplets were collected in a beaker containing 150 mL of a stirred solution of 0.1 M CaCl₂.

Bead formation is driven by the interaction of calcium ions with the G-block regions of the polymer (Badwan et al., 1985) that complexes the calcium ions like egg box system (Rendevski and Andonovski, 2005; Roger et al., 2006).

After 8 h, the beads were filtered, washed with Milli-Q water (4 × 100 mL).

2.3. Adsorption studies

Sorption kinetic and isotherm experiments were conducted in batch mode without pH adjustment (initial pH = final pH = 5.5) by shaking different amounts of alginate composite beads with 10 mL of solution containing different concentrations of PCBs in mixture (16 single components). Moreover, to compare the adsorption data, adsorption studies were carried out also using alginate beads without montmorillonite. In detail, given the low PCB solubility, solutions with PCB concentrations ranging from 2 to 15 μg L⁻¹ were prepared by placing different volumes of a 1 mg L⁻¹ PCB hexane solution in a beaker containing 0.087 g of NaCl and removing the hexane by heating at 40 °C for 30 min. After hexane evaporation, 10 mL of Milli-Q water was added to each sample together with the alginate montmorillonite beads. It should be noted that, if considered as single components, PCB 5 Cl phase would separate from the aqueous phase at concentrations above 9.8 ppb. The same would occur to PCB 6 Cl at concentrations higher than 3 ppb. However, in the presence of other more soluble PCBs (PCB 3 Cl and PCB 4 Cl) the solubility of PCB 5 Cl and PCB 6 Cl should increase. Indeed, we did not observe any precipitations/phase separations at the highest concentration values (15 ppb of each compound).

A series of batch experiments were conducted to study the effect of parameters influencing the adsorption, such as pH, contact time, amount of adsorbent and initial concentration of adsorbate. All experiments were performed at room temperature (25 ± 1 °C) and in 0.15 M NaCl solution.

Preliminary tests showed that 6 h of equilibration time was sufficient to obtain an equilibrium condition between adsorbent and adsorbate.

At the end of the adsorption process, the beads were easily separated by filtration and the residual amount of PCBs in solution was extracted by liquid–liquid extraction using dichloromethane, according to the
The organic extract was dried and diluted with a solution containing an internal standard. The residual concentration of each single PCB in solution was determined by GC–MS analysis performed using a Shimadzu GC–MS 2000 QP Plus gas-chromatograph equipped with a SLB-5ms (30 m × 0.25 mm I.D., 0.25 μm film thickness) fused-silica capillary column from Supelco SLB-5ms, lot. 41579-03A. Ultra pure (99.999%) helium was used as carrier gas and the flow rate was maintained at 1.7 mL min⁻¹. A concentrated solution was injected using the Shimadzu Auto Injector AOC-20I, in splitless mode with a 0.61 min split delay. The injector was maintained at 250 °C and the detector at 270 °C. The GC temperature ramp increased: from 60 °C (1 min) to 170 °C (1 min) at a 30° min⁻¹ heating rate, from 170 °C to 300 °C at a 5° min⁻¹ rate and then from 300 °C to 330 °C (5 min) at 20° min⁻¹ rate.

The calibration was performed weekly. The data were acquired operating in single-ion monitoring (SIM) mode. Identification of the components of the standard mixture was carried out by comparing retention times for each component in the mixture with those of the corresponding pure compounds analyzed under the same experimental conditions. Identification was confirmed by comparing the corresponding MS spectra.

The sorption capacity of the beads was determined by material mass balance of the initial and equilibrium concentrations of the solution. Adsorption on the glassware was found to be negligible and was determined by running several blank experiments. Each experiment was repeated three times and mean values were considered for the fitting process.

The adsorbed PCB amount for mass unit of adsorbent at equilibrium is reported in Eq. (1):

\[ q_e = \frac{(C_o - C_e)}{mV} \]  

where \( q_e \) (μg g⁻¹) is the amount of PCB adsorbed at equilibrium, \( C_o \) and \( C_e \) are the initial and equilibrium concentrations of PCB solutions (μg L⁻¹), \( V \) is the volume (liters) of the solution and \( m \) is the mass of the adsorbent used (grams).

Table 1
Structure and IUPAC name of single PCB in the mixture.
3. Results and discussion

3.1. Bead characterization

The formation of hybrid beads, such as reported in literature, could be driven by polar interactions between the uncharged siloxane moieties of the clay and the hydroxyl groups of the alginate biopolymer (Cavallaro et al., 2013). Compared to normal alginate beads, the introduction of montmorillonite into alginate capsules was accompanied by a significant change in color of the beads, from uncolored to white, easily detectable by the naked eye.

Fig. 1 shows the FT-IR spectra of calcium alginate beads (Fig. 1, top), montmorillonite (Fig. 1, middle) and alginate montmorillonite beads (Fig. 1, bottom).

The spectrum of Ca-alginate montmorillonite beads is a spectrum mix of alginate and montmorillonite. Differences between alginate montmorillonite beads and alginate beads are detectable at: 3631 cm$^{-1}$ corresponding to OH stretching mode in molecular water and Si–OH; 1044,
3.3. Adsorption kinetic study

The adsorption of PCB mixture was monitored from 1 to 16 h. The percentage of adsorption gradually increased during the first 6 h of contact and remained constant after this time as observed for other organic pollutants in biomaterial beads (Chen et al., 2007).

The relationships between contact times and PCBs in solution adsorption are shown in Fig. 2.

These results could be explained considering that adsorption sites are more numerous and available at the beginning of the experiment.

Kinetic models can be used to determine the mechanism of adsorption and the efficiency of the adsorbents for the removal of pollutants. In this study, the adsorption data of PCBs by alginate–montmorillonite were fitted through two kinetic models including pseudo-first-order and pseudo-second-order. The pseudo-first order kinetic (Trivedi et al., 1973) is shown in Eq. (2).

\[
\ln(q_e - q_t) = \ln(q_e) - k_1t
\]

where \(q_e\) (mg \(\text{g}^{-1}\)) and \(q_t\) (mg \(\text{g}^{-1}\)) are the amounts of PCBs adsorbed on the alginate–montmorillonite beads, at equilibrium and at time \(t\), respectively. \(k_1\) (1 h\(^{-1}\)) is the pseudo-first order rate constant. \(k_2\) and \(q_e\) were determined from the slope and intercept of the linear plot of \(\ln(q_e - q_t)\) vs \(t\), respectively.

The experimental data were also analyzed by pseudo-second order model (Ho and McKay, 1999). This adsorption kinetic is shown by the equation where \(q_e\) and \(q_t\) have the same definition as those of pseudo-first order model. The pseudo-second order kinetic is shown in Eq. (3).

\[
t/q_t = 1/(K_2q_e^2) + t/q_e
\]

Table 2 shows the parameters for different kinetic models. The higher linear correlation coefficient of the pseudo-second order model shows that this kinetic model fitted the data better than other kinetic models described earlier. Moreover, the \(q_e\) calculated (\(\mu\text{g} \text{g}^{-1}\)) using this kinetic model, is reasonably similar to experimental \(q_e\) (\(\mu\text{g} \text{g}^{-1}\)) obtained from experimental data. The pseudo-second order kinetic parameters are presented in Table 1.

### Table 2

<table>
<thead>
<tr>
<th>(C_0) (5 (\mu\text{g} \text{L}^{-1}))</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_1) (min(^{-1}))</td>
<td>(q_e) ((\mu\text{g} \text{g}^{-1}))</td>
<td>(R^2)</td>
<td>(K_2) (g (\mu\text{g}^{-1}) min(^{-1}))</td>
</tr>
<tr>
<td>PCB 3 Cl</td>
<td>0.0147</td>
<td>1.53</td>
<td>0.988</td>
</tr>
<tr>
<td>PCB 4 Cl</td>
<td>0.0131</td>
<td>2.10</td>
<td>0.992</td>
</tr>
<tr>
<td>PCB 5 Cl</td>
<td>0.0117</td>
<td>2.45</td>
<td>0.999</td>
</tr>
<tr>
<td>PCB 6 Cl</td>
<td>0.0106</td>
<td>2.24</td>
<td>0.968</td>
</tr>
</tbody>
</table>
The pseudo-second order rate constant values, $k_2$, ranged from 0.0055 to 0.0220 g μg$^{-1}$ min$^{-1}$.

### 3.4. Effect of adsorbent dose

Effect of adsorbent dose was investigated by monitoring the amount of pollutant adsorbed from alginate–montmorillonite beads as a function of mass. The experiments were carried out increasing the mass of beads from 0.25 g to 2.5 g in the experiments keeping constant the volume (10 mL) and concentrations of PCB mixture (from 3 to 6 chlorination grade) in solutions (10 μgL$^{-1}$).

From Fig. 3, it is evident that PCB percentage removal increases rapidly with the mass of alginate–montmorillonite beads, due to the greater availability of binding sites of the sorbent. Starting from penta-chlorinated PCBs, the adsorption reaches its maximum by using 2.5 g of alginate beads. Moreover, the percentage of removal varies with the chlorination degree.

Comparing adsorption results for PCBs of different chlorination grades, the sorbent showed a higher adsorption capacity for PCBs at low chlorination grade.

The adsorption of PCBs could not be correlated to physical parameters such as solubility and octanol–water partition coefficients. This behavior can be ascribed at different interaction types between PCBs at different chlorination grades and alginate montmorillonite beads. Moreover, Calace et al. (2002) observed the same trend in adsorption of other organic pollutants such as phenols on paper mill sludge.

### 3.5. Adsorption isotherms for PCB mixture in alginate–montmorillonite beads

An adsorption isotherm describes the relationship between the amount of pollutant that is adsorbed on the beads and the concentration of dissolved pollutant in the solution at equilibrium. Several models have been published (Foo and Hameed, 2010) to describe experimental data of adsorption isotherms.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Chapman</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$ (μg g$^{-1}$)</td>
<td>$K$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>PCB 3 Cl</td>
<td>4.74</td>
<td>225.70</td>
<td>0.880</td>
</tr>
<tr>
<td>PCB 4 Cl</td>
<td>7.04</td>
<td>0.85</td>
<td>0.824</td>
</tr>
<tr>
<td>PCB 5 Cl</td>
<td>11.24</td>
<td>0.28</td>
<td>0.885</td>
</tr>
<tr>
<td>PCB 6 Cl</td>
<td>12.39</td>
<td>0.18</td>
<td>0.939</td>
</tr>
</tbody>
</table>

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Fig. 4. Experimental isotherms for PCB adsorption on alginate montmorillonite beads. a) Tri-chlorinated PCB; b) tetra-chlorinated PCB; c) penta-chlorinated; d) hexa-chlorinated PCB.
Langmuir, Freundlich and Chapman isotherm adsorption models were applied to analyze the relationship between the amounts of different PCBs adsorbed on the alginate–montmorillonite beads. The Langmuir isotherm predicts the maximum monolayer adsorption capacity of the adsorbent. The expression of the Langmuir equation is reported in Eq. (4) (Langmuir, 1918):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

where $C_e$ (mg L$^{-1}$) is the adsorbate concentration at equilibrium time, $q_e$ (mg g$^{-1}$) is the adsorption capacity of the adsorbent at equilibrium, $K_L$ (L mg$^{-1}$) is the Langmuir constant and $q_m$ (mg g$^{-1}$) is the maximum monolayer adsorbent capacity (Ho and McKay, 1999). $q_m$ and $K_L$ are obtained from the intercept and slope of linear plot of $C_e q_e$ versus $C_e$, respectively and are shown in Table 3.

The Freundlich isotherm model is usually employed for multilayer adsorption on a heterogeneous adsorbent surface (Koyuncu et al., 2011). The non-linear expression of the Freundlich model is reported in Eq. (5):

$$q_e = K_F C_e^{1/n}.$$  \hspace{1cm} (5)

$K_F$ is the Freundlich constant related to the sorbent capacity of alginate–montmorillonite beads and $n$ is an empirical parameter representing the heterogeneity of site energies.

The Chapman isotherm model is based on the assumption of cooperative interactions between adsorbate molecules. The expression of the Chapman sigmoidal equation is reported in Eq. (6):

$$q_e = q_m \left(1 - e^{-K_C C_e} \right).$$  \hspace{1cm} (6)

The value of $q_m$ in the Chapman equation is related to the sorption capacity of sorbent. The constant terms of the Chapman equation ($q_m, K$ and $C_1$) were obtained from the intercept and slope of the linear plot of $q_e$ versus $C_e$.

| Analyte | Langmuir | | Freundlich | | Chapman |
|---------|----------|-------------------------|-----------|-----------|
|         | $q_m$ (mg g$^{-1}$) | $K$ | $R^2$ | $q_m$ (mg g$^{-1}$) | $K$ | $1/n$ | $R^2$ | $q_m$ (mg g$^{-1}$) | $K$ | $R^2$ |
| PCB 3 CI | 332.56 | 0.29 | 0.991 | - | 83.71 | 0.762 | 0.989 | - | - | - |
| PCB 4 CI | 65.97 | 0.36 | 0.976 | - | 18.19 | 0.662 | 0.985 | - | - | - |
| PCB 5 CI | 54.95 | 0.44 | 0.986 | - | 16.25 | 0.604 | 0.997 | - | - | - |
| PCB 6 CI | 44.94 | 0.40 | 0.977 | - | 12.78 | 0.565 | 0.992 | - | - | - |

Fig. 5. Experimental isotherms for PCB adsorption on alginate beads. a) Tri-chlorinated PCB; b) tetra-chlorinated PCB; c) penta-chlorinated; d) hexa-chlorinated PCB.
of PCB solution adsorption in alginate montmorillonite beads has shown that kinetic mechanism of adsorption best fits with a pseudo second order mechanism. By taking advantage of cooperative adsorption processes, hybrid alginate/montmorillonite beads could be a valid alternative for organic pollutant removal in wastewater treatment.

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References


